Seminarului National de Nanostiinta si Nanotehnologie

Electro-optical Properties of Conjugated Polyrotaxanes Based on Fluorene

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ABSTRACT

The effect of complexation of a poly[2,7-(9,9-dioctylfluorene-*alt*-2,7 fluorene] copolymer into the inner cavity of native or modified cyclodextrin on the electro-optical properties was investigated.

The fluorescence spectra of the polymeric rotaxanes exhibited the blue emission bands arising from the fluorene chromophore units, a longer fluorescence lifetime, and higher semiconducting properties compared with the reference copolymer.

The encapsulation of fluorene copolymer into macrocycle cavities of cyclodextrin was found to positively affect the aggregation in the solid state through the prevention of interchain interactions, while leaving unaltered the desirable electronic properties related to π-conjugation.

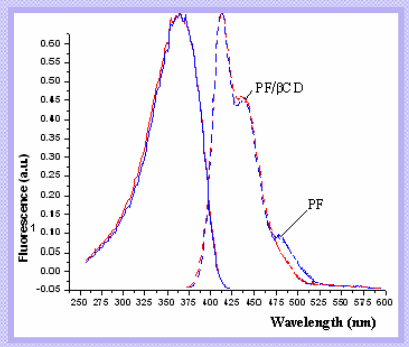
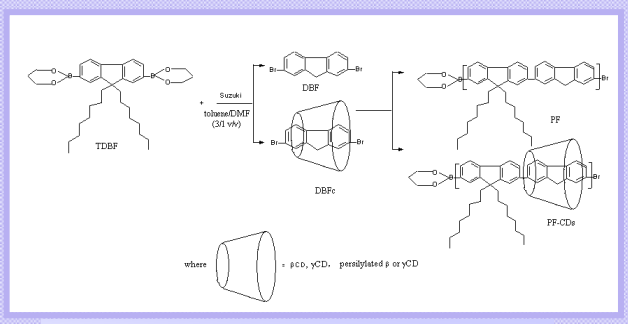


Figure 1. Normalized excitation (λem = 415 nm) and emission (λex = 374 nm) fluorescence spectra of the PF and PF-βCD copolymers in DMF solution



Scheme 1. Synthesis of PF-CD and PF copolymers

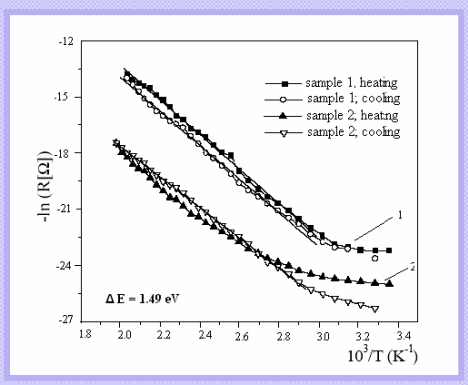


Figure 2. Electrical resistance of PF-γCD copolymer film versus temperature

Tabel 1. Electrochemical Data of the Copolymers

Polymer	E_{ox}^{onset} (V)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gopt} (eV)
PF	1.02	-5.41	-2.48	2.93
PF-βCD	0.75	-5.10	-2.27	2.83
PF-pβCD	0.73	-5.08	-2.19	2.89
PF-γCD	0.99	-5.38	-2.40	2.98

Table 2. Copolymers fluorescence lifetimes

Polymer	Lifetimes (ns)
PF [a]	0.54
PF-pγCD [b]	0.68
PF-βCD [a]	0.62
PF-γCD [a]	0.59

[a] Measured from DMF solution.

[b] Measured from $CHCl_3$ solution

CONCLUSION

***The electro-optical properties of a new class of fluorene copolymers having statistically multiply blocked rotaxane structure on the main chain are presented .**

***The fluorescence spectra of the copolymers exhibited the typical blue emission bands arising from the fluorene chromophore units.**

***The rotaxane copolymer displaced a longer fluorescence lifetime, induced by a partial protection of the macrocycle.**

***The stronger absorption intensity in the rotaxane samples could be indicative of a constructive excitonic coupling among the polymer chain caused by the protection of the macrocycle.**

***The higher semiconductivity of the studied rotaxane copolymers is presumably due to its molecular structure, which affords extended conjugation of the electrons in the copolymer chain and reduces aggregation by partial encapsulation of single polymer chains.**

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